

# Hydration counteracts the separation of lanthanides by solvent extraction

Zheng Li  | Koen Binnemans 

Department of Chemistry, KU Leuven,  
Heverlee, Belgium

## Correspondence

Zheng Li, Department of Chemistry, KU  
Leuven, Celestijnenlaan 200F, B-3001  
Heverlee, Belgium.  
Email: zheng.li@kuleuven.be

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## Abstract

The extraction of lanthanides from aqueous nitrate solutions by quaternary ammonium nitrate ionic liquids (e.g., [A336][NO<sub>3</sub>]) shows a negative sequence (i.e., light lanthanides are more efficiently extracted than heavy lanthanides), which conflicts with the lanthanide contraction. In this study, we explored the origin of the negative sequence by investigating the extraction of lanthanides from ethylammonium nitrate by [A336][NO<sub>3</sub>]. The extraction shows a positive sequence, which is converted to a negative sequence with the addition of water. The transformation from positive to negative sequences reveals that the negative sequence is caused by the hydration of lanthanide ions: hydration of lanthanide ions counteracts the extraction. Therefore, the use of solvents that have weak solvation with lanthanide ions might enhance the separation of the elements by solvent extraction.

## KEYWORDS

Aliquat 336, hydration, ionic liquids, lanthanides, solvent extraction

## 1 | INTRODUCTION

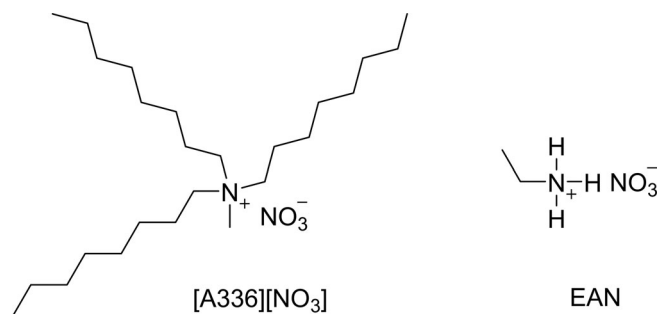
Separation of trivalent rare-earth ions, particularly adjacent lanthanides (Ln(III)), by solvent extraction is challenging due to the similar chemical properties of these elements.<sup>1,2</sup> Because of the lanthanide contraction, the charge density of lanthanide ions increases with increasing atomic number across the lanthanide series, hence the stability of metal complexes should show a similar trend. The extraction of Ln(III) by acidic extractants (e.g., D2EHPA, PC88A) increases with increasing atomic number, showing a positive sequence.<sup>1,3-5</sup> This order reflects the lanthanide contraction. However, the extraction of Ln(III) from aqueous nitrate solutions by nitrate-based ionic liquids (e.g., [A336][NO<sub>3</sub>], a mixture of long-chain quaternary ammonium nitrates, with trioctylmethylammonium nitrate as the main component) decreases with increasing atomic number, showing a negative sequence.<sup>3,6,7</sup> This order is in disagreement with the lanthanide contraction. Recently, the extraction of Ln(III) by [A336]-based ionic liquids has been studied intensively from different perspectives.

Onghena et al.<sup>8</sup> and Hunter et al.<sup>9</sup> studied the speciation of Ln(III) complexes in the organic phase by various analytical, spectroscopic, and computational techniques. Knight et al.<sup>10</sup> explored the extraction of Ln(III) through the aggregation of extractants. Sun et al.<sup>11</sup> investigated the synergism of affinity of anions to Pr(III) and the Hofmeister bias of anions on the extraction of Pr(III). Lovering et al.<sup>12</sup> studied the effect of headgroup-anion interactions at the interface on Ln(III) extraction. These studies provide valuable insights into the mechanism of Ln(III) extraction by [A336]-based ionic liquids, but the origin of the negative sequence is still not understood yet.

Solvent extraction contains two immiscible phases, an organic (less polar) phase containing extractants in a diluent and an aqueous (more polar) phase containing the metal cations to be separated. Although water is the most popular choice for the more polar phase of solvent extraction, several studies have shown that various polar organic solvents can replace water and the substitution of solvents can significantly alter the separation of metals.<sup>13-16</sup> A major reason for the alteration of metal separations by nonaqueous solvent

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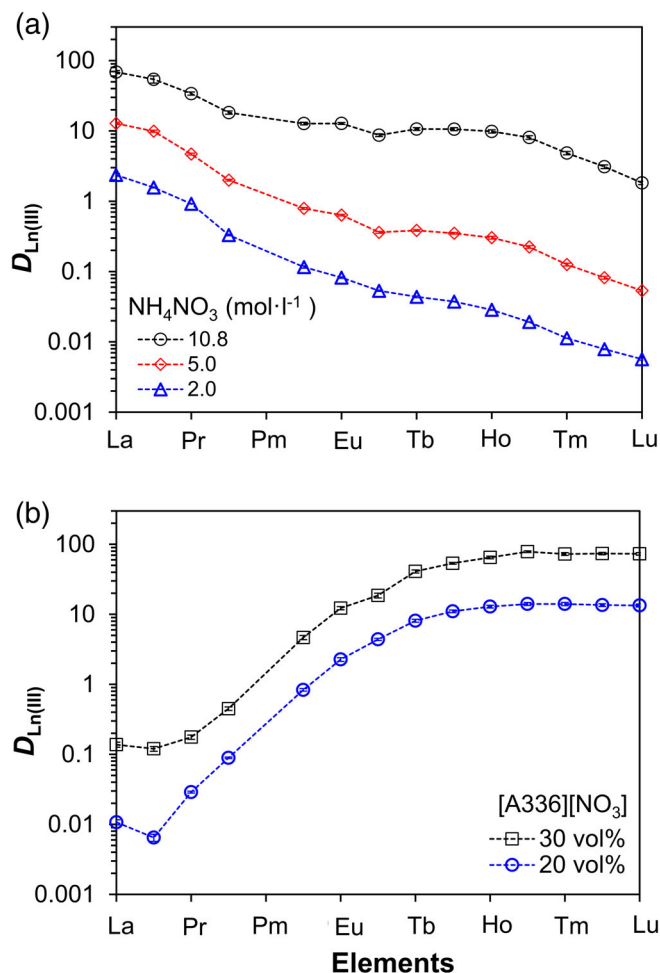
**FIGURE 1** Structures of [A336][NO<sub>3</sub>] (the main component tri-*n*-octylmethylammonium nitrate is shown) and ethylammonium nitrate (EAN)

extraction is because of the change of solvation in the more polar phase.<sup>16</sup> Moreover, hydration of metal ions may also affect the behavior of metals extraction.<sup>17</sup> The high degree of hydration of Ln(III) in aqueous solution was found responsible for the low extraction yield of Ln(III) to the less polar phase as chloridometalate anions.<sup>18</sup> Since studies on the speciation of Ln(III) in the less polar phase have not found the explanation for the negative sequence of Ln(III) extraction by nitrate ionic liquids, one may seek the answer in the hydration (or solvation) behavior of metal ions in the more polar phase. However, it is very difficult to control the extent of hydration of Ln(III) in aqueous solutions because of the strong affinity of lanthanide ions to water molecules. Replacement of water by another polar solvent avoids solvation with water (hydration), but introduces solvation by the new solvent, not simplifying the problem.

In this study, we investigate the origin of the negative sequence exhibited in the extraction of Ln(III) from aqueous nitrate solutions by [A336][NO<sub>3</sub>] (Figure 1) from the perspective of solvation in the more polar phase. Ethylammonium nitrate (EAN, Figure 1) is used as the solvent of the more polar phase to diminish the interference of the solvation of Ln(III) with ligands other than nitrates. EAN is a room temperature ionic liquid (melting point: 12°C). The use of EAN as the solvent of the more polar phase in the solvent extraction of Ln(III) by [A336][NO<sub>3</sub>] avoids the introduction of a new solvating ligand because both the less polar phase and the more polar phase contain nitrates as the only ligand.

## 2 | EXPERIMENTAL

Chemical details are given in Data S1. Water content of [A336][NO<sub>3</sub>] and the EAN solution (containing 14 lanthanide nitrates, each nitrate being 0.005 mol l<sup>-1</sup>) was determined to be 0.44 wt% and <0.10 wt% by a Karl Fischer Coulometer (Mettler-Toledo C30S). Anhydrous toluene (<0.002 wt% water) was used as diluent for the extraction from EAN solution. Each extraction experiment was carried out in a 4-ml glass vial with 2.0 ml of the more polar phase (aqueous or EAN solution) and 2.0 ml of the less polar phase ([A336][NO<sub>3</sub>] in toluene). Mixtures of the two phases were shaken for 30 min at 300 rpm on a Thermo Scientific 2000 shaker to attain extraction equilibrium.

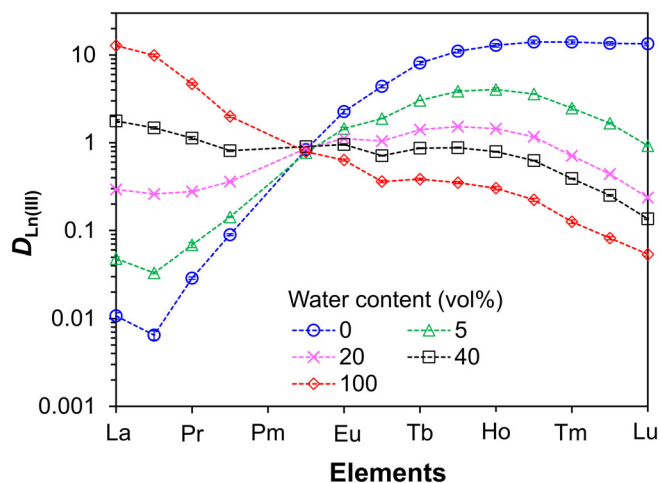


**FIGURE 2** Effect of the  $NH_4NO_3$  concentration (a) and the [A336][NO<sub>3</sub>] concentration (b) on the extraction of Ln(III). The more polar phase was a mixture of 14 lanthanide nitrates (0.005 mol l<sup>-1</sup> of each element, excluding Pm(III)) in either aqueous solutions (a) or in ethylammonium nitrate (EAN) solutions (b); the less polar phase was 20 vol% [A336][NO<sub>3</sub>] (a), and 20 vol% and 30 vol% [A336][NO<sub>3</sub>] in toluene (b) [Color figure can be viewed at wileyonlinelibrary.com]

Afterward, the samples were centrifuged for 3 min at 4,000 rpm in a Heraeus Megafuge 1.0 centrifuge to accelerate phase separation. The loaded less polar phases were stripped with water. Metal concentrations in both the more polar phase and the resultant aqueous solution after stripping were measured by ICP-OES (PerkinElmer Optima 8300). Mutual solubility of the two phases was determined by <sup>1</sup>H NMR spectra (Table S1). All solvent extraction experiments were conducted triplicate at room temperature (21 ± 1°C).

## 3 | RESULTS AND DISCUSSIONS

Extraction of Ln(III) by 20 vol% [A336][NO<sub>3</sub>] in toluene from aqueous nitrate solutions was conducted and a negative sequence was observed (Figure 2a), which is consistent with previous studies.<sup>3,6,8</sup> With an increase in  $NH_4NO_3$  concentration in the aqueous solutions, the extraction of all Ln(III) increased, and the slopes of the lines



**FIGURE 3** Effect of water content on the extraction of Ln(III) ions by [A336][NO<sub>3</sub>]. The more polar phases were mixtures of ethylammonium nitrate (EAN) and aqueous solution (5.0 mol·l<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub>) containing 14 lanthanide nitrates (0.005 mol·l<sup>-1</sup> of each element, excluding Pm(III)); the less polar phase was 20 vol% [A336][NO<sub>3</sub>] in toluene [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

slightly flattened. If we were able to further increase the NH<sub>4</sub>NO<sub>3</sub> concentration in aqueous solutions, a further flattening of the lines would be expected. Unfortunately, 10.8 mol l<sup>-1</sup> is the saturation concentration of NH<sub>4</sub>NO<sub>3</sub> in water at room temperature (22°C).

When water was replaced by EAN (molarity is about 11.2 mol l<sup>-1</sup>), the extraction of Ln(III) by 20 vol% [A336][NO<sub>3</sub>] in toluene showed a surprising positive sequence (Figure 2b), opposite to the extraction from aqueous solutions. The increase of [A336][NO<sub>3</sub>] concentration to 30 vol% obtained the same trend, although the extraction increased for all elements. The extraction increased from Ce(III) to Er(III), where a maximum was reached. This increasing trend is consistent with the lanthanide contraction. The extraction from Er(III) to Lu(III) slightly decreased, which might be due to the effect of a tiny amount of water still present in the system. However, it is very difficult to completely remove the water residue because of the hygroscopicity of ionic liquids. Surprisingly, the extraction of La(III) seems to be an outlier. According to Onghena et al.,<sup>8</sup> La(III) is more likely to bind six bidentate nitrate ions, forming [La(NO<sub>3</sub>)<sub>6</sub>]<sup>3-</sup> in the loaded less polar phase, whereas other Ln(III) ions are likely to coordinate to five nitrate ions, forming [Ln(NO<sub>3</sub>)<sub>5</sub>]<sup>2-</sup>. Coordinating with a higher number of nitrates might be the reason for the relatively higher extraction of La(III).

Upon addition of water to EAN, the extraction of Ln(III) by [A336][NO<sub>3</sub>] gradually converted from the overall positive sequence to a negative sequence (Figure 3). The extraction of the heavy Ln(III) ions is more sensitive to the water content. With only 5 vol% water, the extraction of Er(III), Tm(III), Yb(III), and Lu(III) decreased dramatically, and the decreasing trend from Er(III) to Lu(III) is clearer than exhibited in the extraction from EAN without extra water added. Therefore, we can infer that the extraction of Ln(III) by [A336][NO<sub>3</sub>] increases from Ce(III) to Lu(III) if the extraction system were completely water free.

EAN and [A336][NO<sub>3</sub>] are both nitrate ionic liquids except that the alkyl chains are different. Therefore the Ln(III) ions in both phases can only coordinate with nitrates. With the addition of water, water molecules start to coordinate with Ln(III) ions. The absolute values of the hydration energy of Ln(III) ions increase with increasing atomic number, that is, the same trend as the positive sequence.<sup>19,20</sup> In other words, the hydration of Ln(III) pulls the elements back from being extracted to the [A336][NO<sub>3</sub>] phase, and this pulling force is larger for the element with a higher atomic number. Consequently, the hydration of Ln(III) in aqueous solution counteracts the extraction of Ln(III) ions to the less polar phase. Therefore, the sequence of Ln(III) ions extraction by a certain extractant (acidic, neutral, or basic) is the result of competition between coordination of Ln(III) ions with the extractant and solvation of Ln(III) ions by water (or other polar solvents) in the more polar phase. The extraction of Ln(III) ions by D2EHPA and PC88A is very strong, hence the resulting extraction sequence is the same as the sequence of coordination with the extractant. The same explanation holds for the extraction of Ln(III) ions by the thiocyanate ionic liquid [A336][SCN], which also shows a positive sequence.<sup>6,11</sup> However, the extraction of Ln(III) ions by [A336][NO<sub>3</sub>] is relatively weak, hence the resulting extraction sequence reflects the sequence of hydration. With the addition of NH<sub>4</sub>NO<sub>3</sub> to the aqueous solution, extraction of Ln(III) ions is enhanced due to more nitrates coordinating to Ln(III) in the aqueous solution, hence the extraction sequence would gradually shift from the negative sequence to the positive sequence, as shown in Figure 2a, although the positive sequence was not eventually obtained due to insufficient solubility of NH<sub>4</sub>NO<sub>3</sub> in water. Fortunately, the conversion from the positive sequence of Ln(III) extraction to the negative sequence is clearly shown in Figure 3, by changing the water content of EAN.

Comparing to the extraction of Ln(III) from aqueous solutions (e.g., with 5.0 mol·l<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub>), the extraction from EAN solution has larger separation factors for Ce(III)–Tb(III), but smaller separation factors for Tb(III)–Lu(III). In the extraction of lanthanide nitrates by Cyanex 923, the replacement of water by ethylene glycol as the more polar phase led to improved separation for all elements.<sup>13</sup> Therefore, the change of polar solvents in the more polar phase can considerably change the extraction behavior, and it is a promising approach to improve lanthanides separations by selecting proper polar solvents.

## 4 | CONCLUSIONS

The extraction of Ln(III) nitrates from EAN by the quaternary ammonium nitrate [A336][NO<sub>3</sub>] increases with increasing atomic number, showing a positive sequence, except for La(III). The discrepancy of La(III) from the trend might be explained by differences in coordination chemistry: La(III) is more likely to bind six nitrate ions while other Ln(III) ions are likely to coordinate to five nitrate ions. The positive sequence of Ln(III) extraction complies with the lanthanide contraction. The addition of water to EAN gradually transforms the positive sequence to a negative sequence, which is observed for the extraction

of Ln(III) from aqueous nitrate solutions. The comparison of the two opposite sequences reveals that hydration of Ln(III) counteracts the extraction of Ln(III) because the absolute hydration energy of Ln(III) ions increases with increasing atomic number. This discovery stresses the important role of the more polar phase in the solvent extraction of Ln(III) and indicates that the use of solvents that weakly solvate Ln(III) may enhance the separation of Ln(III). This study illustrates the usefulness of working with nonaqueous solvents as the more polar phase in solvent extraction systems.<sup>21</sup>

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## CONFLICT OF INTEREST

The authors declare no conflict of interest.

## ORCID

Zheng Li  <https://orcid.org/0000-0002-7882-5999>

Koen Binnemans  <https://orcid.org/0000-0003-4768-3606>

## REFERENCES

1. Qi D. Chapter 2: Extractants used in solvent extraction–separation of rare earths: extraction mechanism, properties, and features. *Hydrometallurgy of rare earths*. Amsterdam, The Netherlands: Elsevier; 2018:187-389.
2. Xie F, Zhang TA, Dreisinger D, Doyle F. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner Eng*. 2014;56:10-28.
3. Preston JS, Du-Preez AC. Solvent extraction processes for the separation of rare earth metals. In: Sekine T, ed. *Solvent extraction 1990*. Amsterdam, The Netherlands: Elsevier; 1992:883-894.
4. Sato T. Liquid-liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorus compounds. *Hydrometallurgy*. 1989;22(1):121-140.
5. Ma E, Yan X, Wang S, Long H, Yuan C. Solvent extraction of lanthanides by 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester. *SciChina*. 1981;11(5):565-573.
6. Larsson K, Binnemans K. Separation of rare earths by split-anion extraction. *Hydrometallurgy*. 2015;156:206-214.
7. Larsson K, Binnemans K. Separation of rare earths by solvent extraction with an undiluted nitrate ionic liquid. *J Sustain Metall*. 2017;3(1):73-78.
8. Onghena B, Papagni E, Souza ER, Banerjee D, Binnemans K, Vander Hoogerstraete T. Speciation of lanthanide ions in the organic phase after extraction from nitrate media by basic extractants. *RSC Adv*. 2018;8(56):32044-32054.
9. Hunter JP, Dolezalova S, Ngwenya BT, Morrison CA, Love JB. Understanding the recovery of rare-earth elements by ammonium salts. *Metals*. 2018;8(6):465-477.
10. Knight AW, Chiarizia R, Soderholm L. Extraction selectivity of a quaternary alkylammonium salt for trivalent actinides over trivalent lanthanides: does Extractant aggregation play a role? *Solvent Extr Ion Exch*. 2017;35(4):266-279.
11. Sun P, Huang K, Liu H. The nature of salt effect in enhancing the extraction of rare earths by non-functional ionic liquids: synergism of salt anion complexation and Hofmeister bias. *J Colloid Interface Sci*. 2019;539:214-222.
12. Lovering K, Nayak S, Bu W, Uysal A. The role of specific ion effects in ion transport: the case of nitrate and thiocyanate. *J Phys Chem C*. 2020;124(1):573-581.
13. Batchu NK, Vander Hoogerstraete T, Banerjee D, Binnemans K. Non-aqueous solvent extraction of rare-earth nitrates from ethylene glycol to n-dodecane by Cyanex 923. *Sep Purif Technol*. 2017;174:544-553.
14. Batchu NK, Dewulf B, Riaño S, Binnemans K. Development of a solvommetallurgical process for the separation of yttrium and europium by Cyanex 923 from ethylene glycol solutions. *Sep Purif Technol*. 2020;235:116193.
15. Li Z, Li X, Raiguel S, Binnemans K. Separation of transition metals from rare earths by non-aqueous solvent extraction from ethylene glycol solutions using Aliquat 336. *Sep Purif Technol*. 2018;201:318-326.
16. Li Z, Zhang Z, Smolders S, et al. Enhancing metal separations by liquid-liquid extraction using polar solvents. *Chem A Eur J*. 2019;25(39):9197-9201.
17. Lommelen R, Vander Hoogerstraete T, Onghena B, Billard I, Binnemans K. Model for metal extraction from chloride media with basic extractants: a coordination chemistry approach. *Inorg Chem*. 2019;58(18):12289-12301.
18. Doidge ED, Carson I, Love JB, Morrison CA, Tasker PA. The influence of the Hofmeister bias and the stability and speciation of chloridolanthanates on their extraction from chloride media. *Solvent Extr Ion Exch*. 2016;34(7):579-593.
19. Cosentino U, Villa A, Pitea D, Moro G, Barone V. Extension of computational chemistry to the study of lanthanide(III) ions in aqueous solution: implementation and validation of a continuum solvent approach. *J Phys Chem B*. 2000;104(33):8001-8007.
20. Regueiro-Figueroa M, Esteban-Gómez D, de Blas A, Rodríguez-Blas T, Platas-Iglesias C. Understanding stability trends along the lanthanide series. *Chem A Eur J*. 2014;20(14):3974-3981.
21. Binnemans K, Jones PT. Solvommetallurgy: an emerging branch of extractive metallurgy. *J Sustain Metall*. 2017;3(3):570-600.

## SUPPORTING INFORMATION

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